

A PROCESS DEVELOPMENT PLANT FOR TESTING OF THE MEYERS PROCESS

L.J. Van Nice, E.P. Koutsoukos, R.A. Orsini and R.A. Meyers

TRW Systems and Energy
Redondo Beach, CA 90278

I. INTRODUCTION

Low organic sulfur coal can be desulfurized prior to combustion using the Meyers Process(1,2) to meet governmental requirements for sulfur oxide emissions.

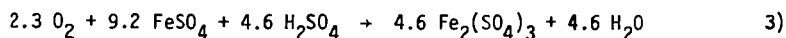
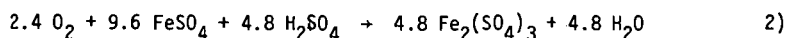
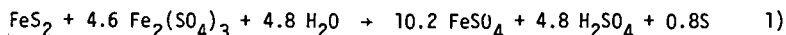
The process removes up to 80 percent of the total sulfur content of coal through chemical leaching of 90 to 95 percent of the pyritic sulfur contained in the coal matrix with aqueous ferric sulfate solution at temperatures of 90° to 130°C. The ferric sulfate content of the leach solution is regenerated at similar temperatures using air or oxygen, and elemental sulfur and iron sulfates are recovered as reaction products or alternatively gypsum can replace a portion of the iron sulfates as a product. The physical form of the coal remains unchanged; only pyrite and some inorganic materials are removed.

The Environmental Protection Agency estimates that 90×10^9 tons (82×10^9 metric tons) of coal reserves in the U.S. Appalachian Coal Basin can be reduced in sulfur content by the Meyers Process to levels which will meet New Source Performance Standards. Successful bench-scale testing(3,4) and promising engineering analyses(3,5-7) together with applicability testing(8,9), have led the Environmental Protection Agency to sponsor the construction and operation of a test plant.

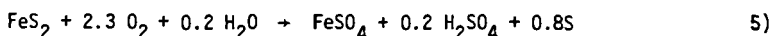
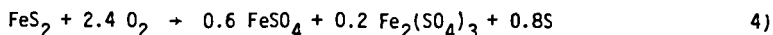
Process chemistry, and test plant design and operation will be described below.

II. PROCESS CHEMISTRY, KINETICS AND SCHEME

The process is based on the oxidation of coal pyrite with ferric sulfate solution (Equation 1). The leaching reaction is highly selective to pyrite with 60 percent of the pyritic sulfur converted to sulfate sulfur and 40 percent to elemental sulfur. The reduced ferric ion is regenerated by oxygen or air according to Equations 2 or 3.



Regeneration can be performed either concurrently with coal pyrite leaching in a single operation or separately. The net effect of the process is the oxidation of pyrite with oxygen to yield recoverable iron, sulfate sulfur, and elemental sulfur. The form of process products varies to some extent with the degree of regeneration performed. Thus, Equations 1 and 2 lead to the overall process chemistry indicated by Equation 4 with the products being a mixture of iron sulfates and elemental sulfur. Equations 1 and 3 yield ferrous sulfate, sulfuric acid, and elemental sulfur as indicated by Equation 5.



Several options exist in product recovery. Iron sulfates may be recovered as pure solids by stepwise evaporation of a spent reagent slipstream with ferrous sulfate being recovered first because of its lower solubility. Alternately, ferrous sulfate may be recovered by crystallization and ferric sulfate or sulfuric acid removed by liming spent reagent or spent wash water slipstreams. Iron sulfates may be stored as such for sale or may easily be converted to highly insoluble basic iron sulfates (by air oxidation) or calcium sulfate (by low-temperature solid phase reaction) for disposal. Elemental sulfur may be recovered from coal by vaporization with steam or by vacuum or it can be leached out with organic solvents such as toluene. Product marketability and product recovery economics will dictate the choice. Recovery economics may be influenced by quantity and concentration of product in the process effluent streams which in turn are influenced by the pyrite concentration in the coal and the desired extent of desulfurization.

The process has been extensively studied at bench-scale. Parameters investigated included coal top-size, reagent composition, slurry concentration, reaction temperature and pressure, and reaction time. Additional investigations completed or underway include concurrent coal leaching-reagent regeneration, product recovery, product stability, and the effect of coal physical cleaning on process performance and economics. The process scheme depicted in Figure 1 is based on the bench-scale testing. Coal is a) crushed to the desired size for processing, b) contacted with hot recycled reagent in the Mixer (90-100°C), c) leached of pyrite in the Reactor(s) with simultaneous or separate reagent regeneration, d) washed with hot water, and e) stripped of elemental sulfur, dried and finally cooled. The iron and sulfate sulfur are recovered from spent reagent slipstreams prior to reagent recycle. Figure 2 shows typical data on pyrite removal rates from Appalachian coal as a function of temperature. Removal of 10-20 percent of the pyrite is obtained during slurry mixing and heat-up.

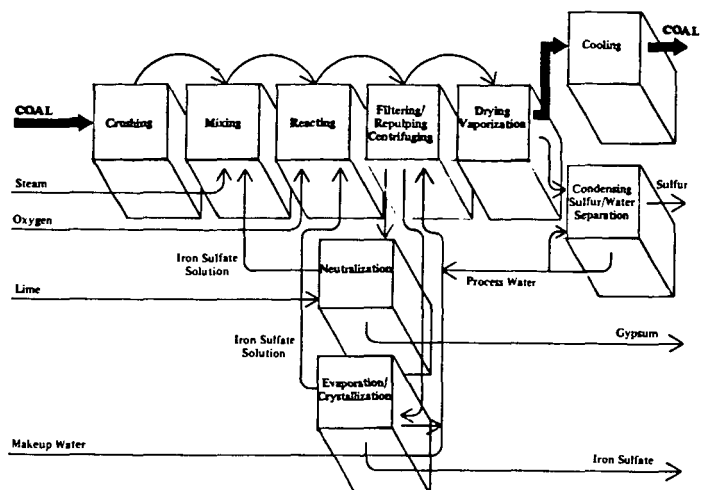


Figure 1. Process Flow Schematic

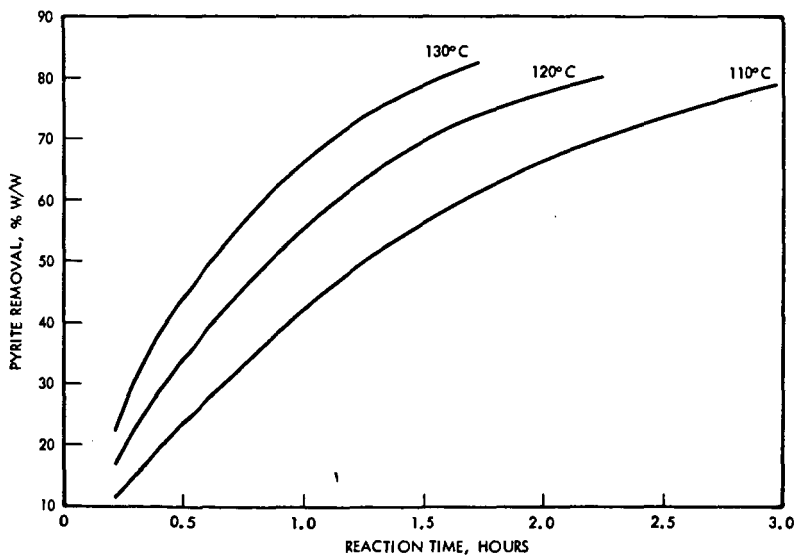


Figure 2. Temperature Effect on Processing of 14 Mesh Top-Size Lower Kittanning Coal (33% w/w Slurries)

Bench-scale data indicated that the pyrite leaching rate from coal can be adequately represented by the empirical rate expression (Equation 6).

$$r_L = - \frac{dW_p}{dt} = K_L W_p^2 Y^2 \quad (6)$$

where

$$K_L = A_L \exp (-E_L/RT),$$

$$W_p = \text{wt percent pyrite in coal,}$$

$$Y = \text{ferric ion-to-total iron ratio in the reactor reagent, and}$$

$$A_L \text{ and } E_L \text{ are constants for each coal and particle size at least over most of the reaction range.}$$

The leach rate is a function of coal type. Pyrite extraction rates vary considerably as detailed in a study of the Meyers Process as applied to U.S. coals(9) - e.g., there was more than one order of magnitude difference between the fastest and slowest reacting coal in attaining 75 percent pyrite removal at 100°C. The reagent regeneration rate is governed by the rate expression (Equation 7).

$$r_R = - \frac{dFe^{+2}}{dt} = K_R P_{O_2} (Fe^{+2})^2 \quad (7)$$

where

$$K_R = A_R \exp (-E_R/RT),$$

$$P_{O_2} = \text{oxygen partial pressure,}$$

$$Fe^{+2} = \text{ferrous ion concentration in the reagent solution, and}$$

$$A_R \text{ and } E_R \text{ are constants.}$$

Engineering evaluation of available data shows that it is preferable to process fine coal (< 2mm top-size) under simultaneous leaching-regeneration conditions in the temperature range of 110-130°C until the majority of the pyrite is leached out. Ambient pressure processing (approximately 100°C) is indicated for the removal of the last few tenths percent of pyrite since the low W_p value substantially reduces the rate of ferric ion consumption and, therefore, the need for simultaneous reagent regeneration. Ambient pressure processing appears to be indicated also for coarse coal (e.g., 10 millimeter top-size) for several reasons. It is difficult to continuously feed a non-slurryable coal into and remove it from a pressure vessel. It is much easier and less costly to drain leach solution from the coal and pump it into a small pressure vessel for regeneration. Also the

slower reaction rate with coarse coal would require much longer residence times and unreasonably large total volume for the pressure vessels. These engineering evaluations were part of the data used to design the test plant.

III. TEST PLANT DESIGN AND OPERATION

A test plant sized to process up to 8 metric tons per day of coal is being built, under the sponsorship of Environmental Protection Agency at TRW's Capistrano Test Site. A plant flow diagram is shown in Figure 3. The facility will be capable of on-line evaluation of the following critical process operations:

- Pressure leaching of pyritic sulfur from 150 micron to 2 mm top-size coal at pressures up to 100 psig,
- Regeneration of ferric sulfate both separately, for processing larger top-size coal or low pyrite coal, and in a single vessel with the leaching step for processing of suspendable coal,
- Filtration of leach solution from reacted coal,
- Washing of residual iron sulfate from the coal.

Iron sulfate crystallization, elemental sulfur recovery and coal-drying unit operations will be evaluated in an off-line mode in equipment vendor pilot units. Leaching of 10 mm top-size coal can be evaluated in an off-line mode in an atmospheric pressure vessel installed in the test plant. Coarse coal processing (5-10 mm top-size) has been very promising in laboratory tests⁽³⁾. If this approach proves out in bench-scale evaluations, more extensive and on-line coal leaching units can be readily added to the present test plant. Processing fine coal allows the highest rate of pyritic sulfur removal, while processing coarse coal, although slower, allows lower cost coal dewatering units and the direct shipping of desulfurized coal product without need for pelletizing.

The test plant under construction at the Capistrano Test Site is a highly flexible facility capable of testing the numerous alternate processing modes of potential interest in the Meyers Process. The flow diagram shown in Figure 3 presents an equipment train for continuous process testing of slurried coal. Fine coal ground to the desired size is stored under nitrogen gas in 1.8 metric ton sealed bins. As required, bins are emptied into the feed tank (T-1). Dry coal is continuously fed by a live bottom feeder to a weigh belt which discharges through a rotary valve to the three stage mixer (Stream 1). The aqueous iron sulfate leach solution (Stream 2) enters the mixer after first passing through a foam breaker (T-2). Steam is added (Stream 3) to raise the slurry to its boiling point. Foaming will occur in the early stages of mixing, but will cease when particle wetting is complete. It is believed that the mixing time and conditions necessary to complete the wetting and defoaming of the slurry will depend on the coal type and size and on the residual moisture in the feed coal. To allow study of the mixing parameters, the mixer stages have variable volume, with variable speed agitators and the feed flow rates for coal, leach solution and steam can be varied over wide ranges.

The defoamed slurry (Stream 4) is pumped to a five stage pressure vessel (Reactor 1) in which most of the pyrite removal reaction occurs. Some of the pyrite reaction occurs during mixing, but in the mixer the reaction rate slows rapidly because the remaining pyrite (W_p) decreases and because the ferric iron is rapidly being converted to ferrous iron (Y decreases). The pressure reactor overcomes the decreased rate in two ways. First, it increases the temperature (and pressure) to increase the reaction rate constant. Second, oxygen is introduced under pressure to regenerate ferric iron and maintain a high solution Y . The flow diagram shows that steam and oxygen can be added to any or all of the five stages and that cooling can be provided for any stage if necessary to remove the excess heat of reaction. The unused oxygen saturated with steam (Stream 7) is contacted in a small pressure vessel (T-3) with the feed leach solution (Stream 5) to provide heated leach solution for the mixer (Stream 2) and cooled vent gas. The vent gas from both T-2 and T-3 are scrubbed in T-4 to remove any traces of acid mist. The reaction parameters of importance have already been well studied at laboratory and bench-scale in batch mode. The test plant reactor will accommodate the necessary studies of key parameters in a continuous reactor at coal throughputs between 2 and 8 metric tons per day. Parameters which will be studied include: temperature, pressure, oxygen purity, slurry concentration, iron sulfate concentration, acid concentration, residence time per stage, number of stages, mixing energy, type of mixing, coal size and type. The reactor can also be used to study leach solution regeneration in the absence of coal.

Reacted coal slurry (Stream 8) at elevated temperature and pressure is flashed into a gas-liquid separator vessel (T-5). The steam generated (Stream 9) is condensed in T-4 and the condensate plus any entrained acid mist is removed with the water. The residual slurry (Stream 10) is fed to a belt filter. The filtrate, which is regenerated leach solution, is removed from the coal slurry through a vacuum receiver (T-9) and pumped (Stream 12) to a large leach solution storage tank (T-6). The coal on the filter belt is washed with water (Stream 11) and discharged from the filter belt. The wash water is removed through a vacuum receiver (T-10) and sent to a large liquid-waste holding tank (T-8) for subsequent disposal. The filter is a highly versatile unit which should provide the data necessary for scale-up. It has variable belt speed, variable belt areas assigned to washing, variable cake washing rates, belt sprays if needed to control blinding of the pores in the belt, and steam nozzles to provide for partial cake drying.

As an alternate process step, the slurry from the flash tank (T-5) can be passed into a secondary reaction vessel (Reactor 2). At typical coal feed rates, this vessel can be filled in about two hours and then closed off, stirred and heated for any desired period of time before being pumped to the filter. Residence times up to about 10 hours are available in the primary reactor, Reactor 1. This secondary reactor can be used to extend residence times to much longer times for examining the removal of final traces of pyrite or examining any other long term behavior. The stirred vessel also can serve to repulp the filter cake for additional coal washing studies.

The final item of major equipment in the test plant is the coarse coal contact vessel (Reactor 3). This insulated and heated tank will hold a full bin (about 1.8 metric tons) of coarse coal (5 to 10 millimeter top-size). The principle use for this vessel is to convert the regenerated leach solution in storage tank T-6 to a more depleted solution in the process feed tank, T-7. In general, the iron sulfate leach solution in the filtrate going to tank T-6 will have a high Y because no secondary reactor was in use. For some test conditions, the feed to the process must be at a lower Y to simulate recycle leach solution from a secondary reactor. Passing all or some portion of the solution through coal will lower the Y of the solution to the desired value. This vessel is basically a coarse coal reactor and if appropriate sampling ports and possibly some flow distribution internals were added, it could be used to obtain design data for coarse coal processing.

Solution tanks are sized at about 50,000 liters to provide for about a week of continuous operation on the same feed without recycle or change. It also provides for uniform leach solution and coal samples of a large enough size for product recovery studies performed by equipment vendors. Operation at the scale of the test plant will provide experience and data expected to be adequate for the design of a demonstration-size commercial plant.

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